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## DESCRIPTION

## EXTERNAL PREPARATION FOR SKIN

## 5 CROSS-REFERENCE TO RELATED APPLICATIONS

This is an application filed pursuant to 35 U.S.C. Section 111(a) with claiming the benefit of U.S. provisional application Serial No. 60/560,607 filed April 9, 2004 under the provision of 35 U.S.C. 111(b), pursuant to 35 U.S.C. Section 119(e) (1).

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## TECHNICAL FIELD

The present invention relates to a novel external preparation for skin. Specifically, the present invention relates to an external preparation for skin comprising multi-branched polysaccharide derivatives, having an effect of maintaining the skin moisture and turgor.

## BACKGROUND ART

As a compound having an effect on maintaining the moisture of the skin in an external preparation for skin, a moisturizer is often used. A moisturizer is blended in an external preparation for skin for the purpose of preventing moisture from evaporating, controlling the moisture in the skin surface, and imparting a moist feeling as well as moisture. The moisture amount in the corneum layer of the skin closely relates to a protective function against a variety of stimuli from the surroundings, and plays an important role in anti-aging of the skin, or a feeling such as a moist feeling or a smooth feeling. This moisture retention in the corneum layer is generally controlled by NMF (natural moisturizing factor) and sebaceous membrane, however, its function is decreased easily due to aging or a stimulus from the surroundings. Therefore, to

replenish a moisturizing component thereof is one of the important factors for an external preparation for skin, in particular a cosmetic product. Examples of the moisturizing component for replenishing moisture to the skin include, as the same biological 5 component or an analogous component, an amino acid, peptide, protein, saccharide, polysaccharide, lipid, glycoprotein and the like.

For example, a cosmetic containing a dipeptide such as alanylglutamine blended therein (JP-A-08-325131), a cosmetic containing a saccharide such as plant-derived 10 glycogen (JP-A-11-180818), and a cosmetic containing mucopolysaccharide blended therein with plant-derived glycogen (JP-A-2001-89381) are known. However, these cosmetics involve disadvantages that amino acid contained therein gives heavy feeling to the skin and does not easily fit in with the skin, and 15 that a dipeptide, in form of a low molecular weight compound having a high solubility, may easily solve out from the external preparation having been applied onto the skin. In addition, a polysaccharide such as glycogen or mucopolysaccharide is not suitably employed as an ingredient for skin external preparations since its 20 straight-chain structure rather causes uncomfortable taut feeling to the skin when the skin is dry, while such a polysaccharide is generally blended in external preparations as material having high moisture retention and skin compatibility. Moreover, a property for retaining skin moisture and turgor for a sufficient length 25 of time against fluctuations in temperature and humidity and sweating cannot be achieved by cosmetics containing such a conventional ingredient. Further, there has been proposed an aqueous cosmetic using microorganism-derived polysaccharide (JP-A-2002-53426). However, polysaccharides derived from natural 30 substances like those mentioned above consist of multiple types of monosaccharide with a variety of composing ratios and structures,

and therefore the diversity makes the quality control of the cosmetic difficult. Moreover, such a cosmetic involves a problem that aggregation often occurs to make the components uneven and generate gelation and/or precipitation, which causes uncomfortable feeling 5 when applied onto the skin. As other moisture retaining agents, polyalcohols such as glycerin, propylene glycol and butylene glycol are used, and these compounds not only retain moisture but also have influences on feeling upon using the cosmetic.

Animal-derived compounds such as proteins such as collagen 10 and keratin and hydrolysates thereof and placenta essence extracted from bovine placenta are also used as moisturizers in some cases, however, due to the decreased reliance on the safety, as more and more countries tend to prohibit uses of such animal-derived compounds in external preparations for skin, the industrial world 15 is shifting toward compounds which have safer origins.

#### DISCLOSURE OF INVENTION

An object of the present invention is to provide an external preparation for skin which can give sufficient moisture and turgor 20 to the skin. For the purpose of attaining the object, the present invention provides an external preparation for skin having high moisture retention property with little moisture eluting out therefrom so that the skin can keep sufficient moisture, giving no uncomfortable taut feeling upon using it even when the skin 25 is in a dry state, being uniform in the structure and components and easy to control the quality, and having safe ingredients so that the external preparation can be used with ease from the viewpoint of safety. More specifically, an object of the invention is to provide an external preparation for skin containing a 30 multi-branched polysaccharide and/or a derivative thereof which is a synthetic polymer derived from anhydrosaccharide.

As a result of intensive investigations to solve this problem, the present inventors have found out that by blending a multi-branched polysaccharide and/or a derivative thereof which consists of saccharides as constituting unit in an external preparation for skin, the external preparation for skin can have properties of giving sufficient moisture to the skin, and can be remarkably improved in adhesion to and affinity for the skin, providing a comfortable touch to the skin even in a dry condition, and thus completed the present invention.

Accordingly, the invention relates to the following items.

[1] An external preparation for skin, which comprises a multi-branched polysaccharide derivative with multi-branched polysaccharide skeleton consisting of saccharides as constituent units, wherein at least one of hydroxyl(OH) groups in the multi-branched polysaccharide skeleton is substituted by OR (wherein R represents a hydrogen atom, a hydrocarbon having 1 to 30 carbon groups or a hydrocarbon having 1 to 30 carbon groups which has hetero atom).

[2] The external preparation for skin according to [1], wherein the multi-branched polysaccharide skeleton comprises a polymer consisting of monomers of anhydrosaccharide and/or anhydrosaccharide derivative in which at least one hydroxyl(OH) group is substituted by OR (wherein R represents a hydrogen atom, a hydrocarbon having 1 to 30 carbon groups or a hydrocarbon having 1 to 30 carbon groups which has hetero atom).

[3] The external preparation for skin according to [2], wherein the anhydrosaccharide or the anhydrosaccharide moiety in the anhydrosaccharide derivative is at least one compound selected from the group consisting of 1,6-anhydrosaccharide, 1,4-anhydrosaccharide, 1,3-anhydrosaccharide, 1,2-anhydrosaccharide and 5,6-anhydrosaccharide.

[4] The external preparation for skin according to [2], wherein the polymer is obtained by cation polymerization or anion polymerization.

[5] The external preparation for skin according to [1], wherein 5 the branching degree of the multi-branched polysaccharide is 0.05 to 1.00.

[6] The external preparation for skin according to any one of [1] to [5], wherein the amount of the multi-branched polysaccharide contained therein is 0.1 to 80 mass %.

10 [7] A cosmetic comprising the external preparation for skin according to any one of [1] to [6].

[EFFECTS OF THE INVENTION]

By using a multi-branched polysaccharide derivative, which consists of saccharides as constituting units, an external 15 preparation for skin which gives sufficient moisture to the skin, with improved adhesion to and affinity for the skin, to thereby retain skin moisture and skin turgor and provide a comfortable touch of the skin even in a dry condition, can be obtained.

20 DETAILED DESCRIPTION OF THE INVENTION

Any multi-branched polysaccharide can be used to constitute the skeleton of the multi-branched polysaccharide derivative according to the present invention without particular limitation so long as the polysaccharide is a compound composed of one or 25 more types of saccharides. The compound has a structure where one single saccharide molecule containing multiple hydroxyl groups has three or more moieties for bonding with adjacent molecules, and thereby the compound structure is formed into a tree like structure having many branching points. Generally, many of 30 polysaccharides existing as natural products are straight-chain polysaccharides or polysaccharaides having not so many branching

points, both types having a main chain. In the multi-branched polysaccharide, with so many branching points being present therein, there is no clearly distinguishable main chain.

Examples of the saccharide constituting the multi-branched polysaccharide of the present invention may include, for example, 5 as a pentose, ribose and deoxyribose, as a hexose, glucose, fructose, galactose and the like.

As a production method of the multi-branched polysaccharide of the present invention, a conventionally known method can be 10 applied. For example, as a production method by a chemical synthesis method, a production method of obtaining a multi-branched polysaccharide by polymerizing a derivative of a monosaccharide as a monomer can be exemplified. Examples thereof include, as disclosed in JP-A-2003-252904, a production method of obtaining 15 a multi-branched polysaccharide by ionic polymerization using an anhydrosaccharide as a monomer.

In this case, examples of the anhydrosaccharide may include 1,6-anhydrosaccharide, 1,4-anhydrosaccharide, 20 1,3-anhydrosaccharide, 1,2-anhydrosaccharide, 5,6-anhydrosaccharide, etc., and a derivative thereof. Specific examples may include 1,6-anhydro- $\beta$ -D-glucopyranose, 1,6-anhydro- $\beta$ -D-mannopyranose, 1,6-anhydro- $\beta$ -D-galactopyranose, 25 1,6-anhydro- $\beta$ -D-allopyranose, 1,6-anhydro- $\beta$ -D-altropyranose, 1,4-anhydro- $\beta$ -D-ribopyranose, 1,4-anhydro- $\alpha$ -D-xylopyranose, 1,4-anhydro- $\alpha$ -L-arabinopyranose, 1,4-anhydro- $\alpha$ -D-lyxopyranose, 30 1,3-anhydro- $\beta$ -D-glucopyranose, 1,3-anhydro- $\beta$ -D-mannopyranose, 1,2-anhydro- $\alpha$ -D-glucopyranose, 1,2-anhydro- $\beta$ -D-mannopyranose, 5,6-anhydro- $\alpha$ -D-glucopyranose, etc., and a derivative thereof.

In addition, as the ionic polymerization, cation 35 polymerization and anion polymerization can be exemplified. Further, there is a production method of obtaining a multi-branched

polysaccharide by using an animal, plant or microorganism, or by using a method of raising, cultivating or culturing it. In this case, a multi-branched polysaccharide with a desired branching degree can be directly used. However, as disclosed in 5 JP-A-8-41104, for example, by a method for producing a multi-branched polysaccharide having an increased branching degree, a branched polysaccharide may become a multi-branched polysaccharide.

The multi-branched polysaccharide derivative of the present 10 invention has a structure in which part and/or all of the hydroxyl groups in the multi-branched polysaccharide that constitutes the skeleton have been substituted by substituent(s). Examples include a compound in which at least one of the hydroxyl groups (OH) of the multi-branched polysaccharide has been substituted 15 by OR (wherein R represents a hydrogen atom, a hydrocarbon having 1 to 30 carbon atoms, or a hydrocarbon having 1 to 30 carbon atoms which has hetero atom).

Examples of the R may include, for example, a methyl group, ethyl group, propyl group, isopropyl group, butyl group, 20 1-methylpropyl group, 2-methylpropyl group, pentyl group, 1-methylbutyl group, 2-methylbutyl group, 3-methylbutyl group, 1-ethylpropyl group, hexyl group, 1-methylpentyl group, 2-methylpentyl group, 3-methylpentyl group, 4-methylpentyl group, 1-ethylbutyl group, 2-ethylbutyl group, heptyl group, 25 1-methylhexyl group, 2-methylhexyl group, 3-methylhexyl group, 4-methylhexyl group, 5-methylhexyl group, 1-ethylpentyl group, 2-ethylpentyl group, 3-ethylpentyl group, octyl group, 1-methylheptyl group, 2-methylheptyl group, 3-methylheptyl group, 4-methylheptyl group, 5-methylheptyl group, 6-methylheptyl group, 30 1-ethylhexyl group, 2-ethylhexyl group, 3-ethylhexyl group, 4-ethylhexyl group, 1-propylpentyl group, 2-propylpentyl group,

nonyl group, decyl group, undecyl group, 10-undecenyl group,  
dodecyl group, tridecyl group, tetradecyl group, pentadecyl group,  
hexadecyl group, 9-hexadecenyl group, heptadecyl group, octadecyl  
group, isostearyl group, cis-9-octadecenyl group, 11-octadecenyl  
5 group, cis-cis-9,12-octadecadienyl group,  
9,12,15-octadecatrienyl group, 6,9,12-octadecatrienyl group,  
9,11,13-octadecatrienyl group, nonadecyl group,  
2,6,10,14-tetramethyl pentadecyl group, icosanyl group,  
8,11-icosadienyl group, 5,8,11-icosatrienyl group,  
10 5,8,11,14-icosatetraenyl group, 3,7,11,15-tetramethylhexadecyl  
group, heneicosanyl group, docosanyl group, acetyl group, propionyl  
group, isopropionyl group, butyryl group, 1-methylpropionyl group,  
2-methylpropionyl group, valeryl group, 1-methylbutyryl group,  
2-methylbutyryl group, 3-methylbutyryl group, 1-ethylpropionyl  
15 group, hexanoyl group, 2-methylpentanoyl group, 3-methylpentanoyl  
group, 4-methylpentanoyl group, 2-ethylbutanoyl group, heptanoyl  
group, 2-methylhexanoyl group, 3-methylhexanoyl group,  
4-methylhexanoyl group, 2-ethylpentanoyl group, 3-ethylpentanoyl  
group, octanoyl group, 2-methylheptanoyl group, 3-methylheptanoyl  
20 group, 4-methylheptanoyl group, 5-methylheptanoyl group,  
6-methylheptanoyl group, 2-ethylhexanoyl group, 3-ethylhexanoyl  
group, 4-ethylhexanoyl group, 2-propylpentanoyl group, nonanoyl  
group, decanoyl group, undecanoyl group, 10-undecenoyl group,  
dodecanoyl group, tridecanoyl group, tetradecanoyl group,  
25 pentadecanoyl group, hexadecanoyl group, 9-hexadecenoyl group,  
heptadecanoyl group, octadecanoyl group, isostearyl group,  
cis-9-octadecenoyl group, 11-octadecenoyl group,  
. cis,cis-9,12-octadecadienoyl group, 9,12,15-octadecatrienoyl  
group, 6,9,12-octadecatrienoyl group, 9,11,13-octadecatrienoyl  
30 group, nonadecanoyl group, 2,6,10,14-tetramethylpentadecanoyl  
group, icosanoyl group, 8,11-icosadienoyl group,

5,8,11-icosatrienoyl group, 5,8,11,14-icosatetraenoyl group, 3,7,11,15-tetramethylhexadecanoyl group, heneicosanoyl group, docosanoyl group, phosphatidyl group and the like. Further, a compound in which R has been bound with an isocyanate group and  
5 the like are also included.

As the synthetic method of the multi-branched polysaccharide derivative of the present invention, for example, a method of synthesizing a multi-branched polysaccharide derivative by modifying a hydroxyl group of a saccharide with a desired functional group after obtaining a multi-branched polysaccharide for constituting the skeleton, or a method of synthesizing a multi-branched polysaccharide derivative by polymerization after modifying a hydroxyl group of an anhydrosaccharide with a desired functional group to serve as a monomer of a multi-branched polysaccharide may be employed.  
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With regard to the modification of the hydroxyl group, for example, a method by a common esterification reaction using a carboxylic acid derivative can be employed. Specific examples include a method of performing reaction by using carboxylic acid as an acid chloride or a mixed acids anhydride, a method of performing reaction by using carbodiimide, a method of using an acid anhydride and the like. Further, in the case of a compound having an isocyanate group, a modification method of forming an urethane bond by heating or by using a catalyst such as a tin-based catalyst or an amine-based catalyst, and the like can be employed.  
20  
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The branching degree of the multi-branched polysaccharide constituting the skeleton of the multi-branched polysaccharide derivative of the present invention is 0.05 to 1.00, preferably 0.2 to 1.0, more preferably 0.4 to 1.0. The multi-branching degree 30 in this case is generally calculated with Frechet formula as shown below.

Branching Degree = (number of dendritic units + number of polymer ends) / (number of dendritic units + number of polymer ends + number of linear chain units)

5 Examples of the method of blending the multi-branched polysaccharide to be used in the present invention into an external preparation for skin include a method of producing an external preparation for skin by mixing it in as a solid, powder or semisolid, a method of producing an external preparation for skin by mixing 10 it in as an aqueous solution, a method of producing an external preparation for skin by mixing it in as a solution of an alcohol or an appropriate solvent, and a method of producing an external preparation for skin by mixing it in or adding by other known methods.

15 The multi-branched polysaccharide to be used in the present invention can be isolated as, for example, a form of powder, however, a solution obtained in the process of the production can be directly blended in an external preparation for skin.

20 The multi-branched polysaccharide to be used in the present invention, as long as the blending amount does not hinder formation of the external preparation for skin as cosmetics, can be blended in an amount of 0.01 to 100 % by mass, preferably from 0.1 to 80 % by mass, more preferably at 1 to 50 % by mass. If the blending amount is less than 0.01 % by mass based on the external preparation 25 for skin, adhesiveness and affinity to the skin are not sufficient, and a feeling such as a moisturizing feeling to the skin cannot be obtained sufficiently in some cases. It can be blended within such a range that essential functions of the external preparation for skin may not be impaired.

30 The term "external preparation for skin" used in the present invention includes cosmetics, detergents, bath agents, soaps and

the like which are used in direct contact with the skin.

Examples of the external preparation for skin of the present invention include in a wide sense, for example, skin milk, skin cream, foundation cream, massage cream, cleansing cream, shaving cream, cleansing foam, skin lotion, lotion, facial mask, lip rouge, rouge, eye shadow, manicure, soap, body shampoo, hand soap, shampoo, hair conditioner, hair tonic, hair treatment, hair cream, hair spray, hair growth tonic, baldness remedy, hair dye, shmaltz, hair remover, anti-dandruff lotion, toothpaste, artificial teeth adhesive, gargle, permanent wave agent, curling agent, styling agent, ointment, cataplasma, tape, bath agent, adiaphoretic, sun protectant and the like, and any type is included as long as it is used in contact with the skin. In particular, a preferred use of the external preparation for skin of the present invention is a cosmetic product. In addition, the user may be anyone regardless of sex or age. Further, products to be used in contact with the skin of animals other than human are also included.

Examples of the form of the present invention include many forms such as powder, granule, tablet, gel and foam, as well as solid, liquid, semisolid and gas.

In the external preparation for skin of the present invention, as a component other than the multi-branched polysaccharide and or derivative thereof, components generally used in an external preparation for skin can be blended within the range that does not impair the effect of this invention, as needed. Examples of components include compounds blendable in cosmetic products, compounds serving as raw materials for quasi-drug products, drug products and medicinal additives.

Examples of such an ingredient include hydrocarbons such as ozokerite,  $\alpha$ -olefin oligomer, light isoparaffin, light liquid isoparaffin, squalene, squalane, synthetic squalane,

phytosqualane, ceresin, paraffin, polyethylene powder, polybutene, microcrystalline wax, liquid isoparaffin, liquidparaffin, mineral oil and vaseline;

natural waxes such as jojoba oil, carnauba wax, candelilla wax, rice bran wax, shellac, lanolin, mink seaceous wax, spermaceti wax, sugarcane wax, sperm whale oil, beeswax and montan wax, natural fats and fatty oils such as avocado oil, almond oil, olive oil, extra virgin olive oil, sesame seed oil, rice bran oil, rice oil, rice germ oil, corn oil, safflower oil, soybean oil, maize oil, rape seed oil, persic oil, palm kernel oil, palm oil, castor oil, sunflower oil, high oleic sunflower oil, grape seed oil, cotton seed oil, coconut oil, hydrogenated coconut oil, beef tallow, hydrogenated oil, horse oil, mink oil, yolk oil, yolk fat oil, rose hip oil, kukui nut oil, evening primrose oil, wheat germ oil, peanut oil, Camellia japonica oil, Camellia kissioil, cacao butter, Japan wax, beef bone tallow, nest's-foot oil, swine tallow, equine tallow, ovine tallow, shea butter, macadamia nut oil and meadowfoam seed oil;

fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, oleic acid, linoleic acid, linolenic acid,  $\gamma$ -linolenic acid, isostearic acid, 12-hydroxystearic acid, undecylenic acid and coconut oil fatty acid;

higher alcohols such as isostearyl alcohol, octyl dodecanol, hexyl decanol, cholesterol, phytosterol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, behenyl alcohol and cetostearyl alcohol;

alkylglyceryl ethers such as batyl alcohol, chimyl alcohol, serachyl alcohol and isostearyl glyceryl ether;

30 esters such as isopropyl myristate, butyl myristate, isopropyl palmitate, ethyl stearate, butyl stearate, ethyl oleate,

ethyl linoleate, isopropyl linoleate, cetyl caprylate, hexyl laurate, isoctyl myristate, decyl myristate, myristyl myristate, cetyl myristate, octadecyl myristate, cetyl palmitate, stearyl stearate, decyloleate, oleyloleate, cetyl ricinoleate, isostearyl laurate, isotridecyl myristate, isocetyl myristate, isostearyl myristate, octyldodecyl myristate, 2-ethylhexyl palmitate, isocetyl palmitate, isostearyl palmitate, 2-ethylhexyl stearate, isocetyl stearate, isodecyl oleate, octyldodecyl oleate, octyldodecyl ricinoleate, ethyl isostearate, isopropyl isostearate, cetyl 2-ethylhexanoate, cetostearyl 2-ethylhexanoate, stearyl 2-ethylhexanoate, hexyl isostearate, ethylene glycol dioctanoate, ethylene glycol dioleate, propylene glycol dicaprylate, propylene glycol dicaprylate/dicaprate, propylene glycol dicaprate, propylene glycol dioleate, neopentyl 15 glycol dicaprate, neopentyl glycol dioctanoate, glyceryl tricaprylate, glyceryl tri 2-ethyl hexanoate, glyceryl tricaprylate/tricaprate, glyceryl tricaprylate/tricaprate/tristearate, glyceryl triundecylate, glyceryl triisopalmitate, glyceryl triisostearate, trimethylolpropane tri 2-ethylhexanoate, trimethylolpropane 20 triisostearate, pentaerythrityl tetra 2-ethylhexanoate, pentaerythrityl tetramyristate, pentaerythrityl tetraisostearate, diglyceryl tetraisostearate, octyldodecyl neopentanoate, isocetyl octanoate, isostearyl octanoate, 2-ethylhexyl 25 isopelargonate, hexyldecyl dimethyloctanoate, octyldodecyl dimethyloctanoate, 2-ethylhexyl isopalmitate, isocetyl isostearate, isostearyl isostearate, octyldodecyl isostearate, lauryl lactate, myristyl lactate, cetyl lactate, octyldodecyl lactate, triethyl citrate, acetyltriethyl citrate, acetyltributyl 30 citrate, trioctyl citrate, triisocetyl citrate, trioctyldodecyl citrate, diisostearyl malate, 2-ethylhexyl hydroxystearate, di

2-ethylhexyl succinate, diisopropyl adipate, diisobutyl adipate,  
dioctyl adipate, diheptylundecyl adipate, sebacate diethyl,  
diisopropyl sebacate, dioctyl sebacate, cholesteryl stearate,  
cholesteryl isostearate, cholesteryl hydroxystearate,  
5 cholesteryl oleate, dihydrocholesteryl oleate, phytosteryl  
isostearate, phytosteryl oleate, isocetyl 12-stearoyl  
hydroxystearate, stearyl 12-stearoyl hydroxystearate, isostearyl  
12-stearoyl hydroxystearate, polyoxyethylene (3)  
polyoxypropylene (1) cetyl ether acetate, polyoxyethylene (3)  
10 polyoxypropylene (1) isocetyl ether acetate, isononyl isononanoate,  
octyl isononanoate, tridecyl isononanoate and isotridecyl  
isononanoate;

silicone oils such as methyl polysiloxane, methylphenyl  
polysiloxane, methyl hydrogen polysiloxane, methyl  
15 cyclopolysiloxane, octamethyl cyclotetrasiloxane, decamethyl  
cyclopentasiloxane, dodecamethyl cyclohexasiloxane, octamethyl  
trisiloxane, decamethyl tetrasiloxane, tetradecamethyl  
hexasiloxane, highly polymerized methyl polysiloxane,  
dimethylsiloxane-methyl (polyoxyethylene) siloxane-methyl (poly  
20 oxypropylene) siloxane copolymer,  
dimethylsiloxane-methyl (polyoxyethylene) siloxane copolymer,  
dimethylsiloxane-methyl (polyoxypropylene) siloxane copolymer,  
dimethylsiloxane-methylcetyl oxysiloxane copolymer,  
dimethylsiloxane-methyl stearoxysiloxane copolymer, polyether  
25 modified silicone, alcohol modified silicone, alkyl modified  
silicone and amino modified silicone;

polyhydric alcohols such as ethylene glycol, diethylene  
glycol, triethylene glycol, polyethylene glycol, propylene glycol,  
dipropylene glycol, polypropylene glycol, pentanediol, glycerin,  
30 diglycerin, polyglycerin, isoprene glycol, 1,3-butylene glycol,  
3-methyl-1,3-butanediol, 1,3-butanediol, 1,2-pantanediol and

1,2-hexanediol;

saccharides such as mannitol, sorbitol, xylitol, maltitol, erythritol, pentaerythritol, glucose, sucrose, fructose, lactose, maltose, xylose and trehalose;

5 polymers such as sodium alginate, carrageen, agar, furcellaran, guar gum, quince seed, Amorphophalus konjak (arum root) mannan, tamarind gum, tara gum, dextrin, starch, locust bean gum, gum arabic, gum gatti, karaya gum, gum tragacanth, arabinogalactan, pectin, quince, chitosan, curdlan, xanthan gum, 10 gellan gum, cyclodextrin, dextran, pullulan, microcrystalline cellulose, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropylmethyl cellulose, carboxymethyl cellulose, carboxy starch, cationized cellulose, starch phosphate ester, cationized guar gum, 15 carboxymethyl-hydroxypropylated guar gum, hydroxypropylated guar gum, albumin, casein, gelatin, sodium polyacrylate, polyacrylic amide, carboxyvinyl polymer, polyethylene imine, highly polymerized polyethylene glycol, polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl ether, polyacryl amide, acrylic acid 20 copolymer, methacrylic acid copolymer, maleic acid copolymer, vinylpyridine copolymer, ethylene/acrylic acid copolymer, vinyl pyrrolidone based polymer, vinyl alcohol/vinyl pyrrolidone copolymer, nitrogen-substituted acrylamide based polymer, amino modified silicone, cationized polymer, dimethylacryl ammonium 25 based polymer, acrylic acid based anion polymer, methacrylic acid based anion polymer, modified silicone, acrylate/methacrylate alkyl (C 10 to 30) copolymer and polyoxyethylene/polyoxypropylene copolymer;

30 alcohols such as ethanol, isopropyl alcohol, 1-butanol, 2-butanol and benzyl alcohol;

anionic surfactants such as coconut oil fatty acid potassium,

coconut oil fatty acid sodium, coconut oil fatty acid triethanolamine, potassium laurate, sodium laurate, triethanolamine laurate, potassium myristate, sodium myristate, isopropanolamine myristate, potassium palmitate, sodium palmitate,  
5 isopropanolamine palmitate, potassium stearate, sodium stearate, triethanolamine stearate, potassium oleate, sodium oleate, castor oil fatty acids sodium, zinc undecylate, zinc laurate, zinc myristate, magnesium myristate, zinc palmitate, zinc stearate, calcium stearate, magnesium stearate, aluminum stearate, calcium myristate,  
10 magnesium myristate, aluminum dimyristate, aluminum isostearate, polyoxyethylene lauryl ether acetate, sodium polyoxyethylene lauryl ether acetate, polyoxyethylene tridecyl ether acetate, sodium polyoxyethylene tridecyl ether acetate, sodium stearoyl lactate, sodium isostearoyl lactate, sodium lauroyl sarcosine,  
15 coconut oil fatty acid sarcosine, sodium coconut oil fatty acid sarcosine, coconut oil fatty acid sarcosine triethanolamine, lauroyl sarcosine, potassium lauroyl sarcosine, lauroyl sarcosine triethanolamine, oleoyl sarcosine, sodium myristoyl sarcosine, sodium stearoyl glutamate, coconut oil fatty acid acyl glutamic acid, potassium coconut oil fatty acid acyl glutamate, sodium coconut oil fatty acid acyl glutamate triethanolamine, lauroylacyl glutamic acid, potassium lauroylacyl glutamate, sodium lauroylacyl glutamate, lauroylacyl glutamate triethanolamine, myristoylacyl glutamic acid, potassium  
20 myristoylacyl glutamate, sodium myristoylacyl glutamate, stearoylacyl glutamic acid, potassium stearoylacyl glutamate, disodium stearoylacyl glutamate, sodium hydrogenated beef tallow fatty acid acyl glutamate, sodium coconut oil fatty acid/hydrogenated beef tallow fatty acid acyl glutamate, sodium  
25 coconut oil fatty acidmethylalanine, lauroylmethylalanine, sodium lauroyl methylalanine, lauroyl methylalanine triethanolamine,  
30

sodium myristoyl methylalanine, sodium lauroyl methyltaurine,  
potassium coconut oil fatty acid methyltaurine, sodium coconut  
oil fatty acid methyltaurine, magnesium coconut oil fatty acid  
methyltaurine, sodium myristoyl methyltaurine, sodium palmitoyl  
5 methyltaurine, sodium stearoyl methyltaurine, sodium oleoyl  
methyltaurine, sodium alkane sulfonate, sodium tetradecene  
sulfonate, sodium sulfosuccinate dioctyl, disodium lauryl  
sulfosuccinate, sodium coconutoil fatty acid ethyl ester sulfonate,  
sodium lauryl sulfate, triethanolamine lauryl sulfate, sodium cetyl  
10 sulfate, triethanolamine alkyl (11,13,15) sulfate, sodium alkyl  
(12,13) sulfate, triethanolamine alkyl (12,13) sulfate, alkyl  
(12,14,16) ammonium sulfate, diethanolamine alkyl (12 to 13)  
sulfate, triethanolamine alkyl (12 to 14) sulfate, triethanolamine  
alkyl (12 to 15) sulfate, magnesium coconut oil alkyl  
15 sulfate/triethanolamine, lauryl ammonium sulfate, potassium  
lauryl sulfate, magnesium lauryl sulfate, monoethanolamine lauryl  
sulfate, diethanolamine lauryl sulfate, sodium myristyl sulfate,  
sodium stearyl sulfate, sodium oleyl sulfate, triethanolamine oleyl  
sulfate, sodium polyoxyethylene lauryl ether sulfate, sodium  
20 polyoxyethylene (1) alkyl (11,13,15) ether sulfate, triethanolamine polyoxyethylene (1) alkyl (11,13,15) ether sulfate,  
sodium polyoxyethylene (3) alkyl (11 to 15) ether sulfate, sodium  
polyoxyethylene (2) alkyl (12,13) ether sulfate, sodium  
25 polyoxyethylene (3) alkyl (12 to 14) ether sulfate, sodium  
polyoxyethylene (3) alkyl (12 to 15) ether sulfate, sodium  
polyoxyethylene (2) lauryl ether sulfate, sodium polyoxyethylene  
(3) myristyl ether sulfate, sodium higher fatty acid alkanol amide  
sulfate ester, lauryl phosphate, sodium lauryl phosphate, potassium  
30 cetyl phosphate, diethanolamine cetyl phosphate, polyoxyethylene  
oleyl ether phosphate, polyoxyethylene lauryl ether phosphate,

sodium polyoxyethylene lauryl ether phosphate, polyoxyethylene cetyl etherphosphate, sodiumpolyoxyethylene cetyl etherphosphate, polyoxyethylene stearyl ether phosphate, polyoxyethylene oleyl ether phosphate, sodium polyoxyethylene oleyl ether phosphate,  
5 polyoxyethylene alkylphenyl ether phosphate, sodium polyoxyethylene alkylphenyl ether phosphate, triethanolamine polyoxyethylene alkylphenyl ether phosphate, polyoxyethylene octyl ether phosphate, polyoxyethylene (10) alkyl (12,13) ether phosphate, polyoxyethylene alkyl (12 to 15) ether phosphate,  
10 polyoxyethylene alkyl (12 to 16) ether phosphate, triethanolamine polyoxyethylene lauryl ether phosphate and diethanolamine polyoxyethylene oleyl ether phosphate;

cationic surfactants such as dioctylamine, dimethylstearylamine, trilaurylamine, diethylaminoethylamide  
15 stearate, lauryl trimethylammonium chloride, cetyl trimethylammonium chloride, cetyl trimethylammonium bromide, cetyl trimethylammonium saccharin, stearyl trimethylammonium chloride, alkyl (20 to 22) trimethylammonium chloride, lauryl trimethylammonium bromide, alkyl (16,18) trimethylammonium  
20 chloride, stearyl trimethylammonium bromide, stearyl trimethylammonium saccharin, alkyl (28) trimethylammonium chloride, di(polyoxyethylene) oleyl methylammonium (2EO) chloride, dipolyoxyethylene stearyl methylammonium chloride, polyoxyethylene (1) polyoxypropylene (25) diethylmethylammonium  
25 chloride, tri(polyoxyethylene) stearyl ammonium (5EO) chloride, distearyl dimethylammonium chloride, dialkyl (12 to 15) dimethylammonium chloride, dialkyl (12 to 18) dimethylammonium chloride, dialkyl (14 to 18) dimethylammonium chloride, dicocoyl dimethylammonium chloride, dicetyl dimethylammonium chloride,  
30 isostearyllauryl dimethylammonium chloride, benzalkonium chloride, myristyl dimethylbenzyl ammonium chloride, lauryl

dimethyl(ethylbenzyl) ammonium chloride, stearyl dimethylbenzyl ammonium chloride, lauryl pyridinium chloride, cetyl pyridinium chloride, lauroyl cholamino formylmethyl pyridinium chloride, stearoyl cholamino formylmethyl pyridinium chloride, alkyl 5 isoquinolinium bromide, methyl benzethonium chloride and benzethonium chloride;

ampholytic surfactants such as  
2-alkyl-N-carboxymethyl-N-hydroxyethyl imidazolium betaine,  
alkyldiamino ethyl glycine hydrochloride, sodium lauryldiamino 10 ethyl glycine, sodium undecyl hydroxyethyl imidazolium betaine, undecyl-N-carboxymethyl imidazolium betaine, disodium coconut oil fatty acid acyl-N-carboxyethyl-N-hydroxyethyl ethylenediamine, disodium coconut oil fatty acid acyl-N-carboxyethoxyethyl-N-carboxyethyl ethylenediamine, 15 disodium coconut oil fatty acid acyl-N-carboxymethoxyethyl-N-carboxymethyl ethylenediamine, sodium laurylamino propionate, sodium laurylamino dipropionate, triethanolamine laurylamino propionate, sodium palmoil fatty acid acyl-N-carboxyethyl-N-hydroxyethyl ethylenediamine, betaine 20 lauryldimethylamino acetate, betaine coconut oil alkyldimethylamino acetate, betaine stearyl dimethylamino acetate, sodium stearyldimethyl betaine, coconut oil fatty acid amidopropyl betaine, palm oil fatty acid amidopropyl betaine, amidopropyl acetate betaine laurate, amidopropyl betaine ricinoleate, stearyl 25 dihydroxyethyl betaine and lauryl hydroxysulfobetaine;

nonionic surfactants such as polyoxyethylene (10) alkyl (12,13) ether, polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene (3,7,12) alkyl (12 to 14) ether, polyoxyethylene tridecyl ether, polyoxyethylene myristyl ether, 30 polyoxyethylene-sec-alkyl (14) ether, polyoxyethylene isocetyl

ether, polyoxyethylene cetostearyl ether, polyoxyethylene  
(2,10,20) isostearyl ether, polyoxyethylene oleylcetyl ether,  
polyoxyethylene (20) arachyl ether, polyoxyethylene octyldodecyl  
ether, polyoxyethylene behenyl ether, polyoxyethylene octylphenyl  
5 ether, polyoxyethylene nonylphenyl ether, polyoxyethylene  
dinonylphenyl ether, polyoxyethylene (1) polyoxypropylene  
(1,2,4,8) cetyl ether, polyoxyethylene (5) polyoxypropylene  
(1,2,4,8) cetyl ether, polyoxyethylene (10) polyoxypropylene  
(1,2,4,8) cetyl ether, polyoxyethylene (20) polyoxypropylene  
10 (1,2,4,8) cetyl ether, polyoxyethylene polyoxypropylene lauryl  
ether, polyoxyethylene (3) polyoxypropylene (34) stearyl ether,  
polyoxyethylene (4) polyoxypropylene (30) stearyl ether,  
polyoxyethylene (34) polyoxypropylene (23) stearyl ether,  
polyoxyethylene polyoxypropylene cetyl ether, polyoxyethylene  
15 polyoxypropylene decyltetradecyl ether, polyethylene glycol  
monolaurate, ethylene glycol monostearate, polyethylene glycol  
monostearate, polyethylene glycol monooleate, ethylene glycol  
fatty acid ester, self-emulsifying ethylene glycol monostearate,  
diethylene glycol laurate, polyethylene glycol myristate,  
20 polyethylene glycol palmitate, diethylene glycol stearate,  
self-emulsifying polyethylene glycol (2) monostearate,  
polyethylene glycol isostearate, ethylene glycol dioctanoate,  
diethylene glycol dilaurate, polyethylene glycol dilaurate,  
polyethylene glycol (150) dipalmitate, ethylene glycol distearate,  
25 diethylene glycol distearate, polyethylene glycol distearate,  
ethylene glycol dioleate, polyethylene glycol dioleate,  
polyethylene glycol diricinoleate, polyoxyethylene (20) sorbitan  
monolaurate, polyoxyethylene (20) sorbitan monopalmitate,  
polyoxyethylene (6) sorbitan monostearate, polyoxyethylene (20)  
30 sorbitan monostearate, polyoxyethylene (20) sorbitan tristearate,  
polyoxyethylene (6) sorbitan monooleate, polyoxyethylene (20)

sorbitan monooleate, polyoxyethylene (20) sorbitan trioleate,  
polyoxyethylene (20) coconut oil fatty acid sorbitan,  
polyoxyethylene (10 to 80) sorbitan monolaurate, polyoxyethylene  
sorbitan tristearate, polyoxyethylene (20) sorbitan isostearate,  
5 polyoxyethylene (150) sorbitan tristearate, polyoxyethylene  
castor oil, polyoxyethylene hydrogenated castor oil,  
polyoxyethylene (10) hydrogenated castor oil, polyoxyethylene (20)  
hydrogenated castor oil, polyoxyethylene (40) hydrogenated castor  
oil, polyoxyethylene (50) hydrogenated castor oil, polyoxyethylene  
10 (60) hydrogenated castor oil, lipophilic glycerin monostearate,  
lipophilic glycerin monooleate, self-emulsifying glycerin  
monostearate, coconut oil fatty acid glycetyl, glycerin laurate,  
glycetyl myristate, glycetyl isostearate, glycetyl ricinoleate,  
glycetyl monohydroxystearate, glycerin oleate, glycetyl linoleate,  
15 glycetyl erucate, glycetyl behenate, wheat germ oil fatty acid  
glyceride, safflower oil fatty acid glycetyl, hydrogenated soybean  
fatty acid glycetyl, saturated fatty acid glyceride, cotton seed  
oil fatty acid glycetyl, monomyristate glycetyl monoisostearate,  
monotallowate glyceride, monolanolin fatty acid glycetyl, glycetyl  
20 sesquioleate, glycetyl distearate, glycetyl diisostearate,  
glycetyl diarachidate, sorbitan monolaurate, sorbitan  
monopalmitate, sorbitan monostearate, sorbitan monoisostearate,  
sorbitan monooleate, sorbitan sesquistearate, sorbitan  
sesquioleate, sorbitan tristearate, sorbitan trioleate, coconut  
25 oil fatty acid sorbitan, sorbitan isostearate, sorbitan  
sesquiisostearate, sorbitan distearate, diglyceryl isopalmitate,  
poly(4 to 10)glyceryl monolaurate, poly(10)glyceryl monomyristate,  
poly(2 to 10)glyceryl monostearate, poly(2 to 10)glyceryl  
monoisostearate, poly(2 to 10)glyceryl monooleate, diglyceryl  
30 sesquioleate, poly(2 to 10)glyceryl diisostearate, poly(6 to  
10)glyceryl distearate, diglyceryl triisostearate,

poly(10)glyceryl tristearate, poly(10)glyceryl trioleate,  
poly(2)glyceryl tetraisostearate, decaglyceryl pentastearate,  
poly(6 to 10)glyceryl pentaoleate, poly(10)glyceryl heptastearate,  
decaglyceryl decastearate, poly(10)glyceryl decaoleate,  
5 concentrated poly(6)glyceryl ricinoleate, sucrose fatty acid ester,  
coconut oil fatty acid sucrose ester, alkyl glucoside, coconut  
oil alkyl dimethylamine oxide, lauryl dimethylamine oxide,  
dihydroxyethyl lauryl dimethylamine oxide, stearyl dimethylamine  
oxide, oleyl dimethylamine oxide and polyoxyethylene coconut oil  
10 alkyl dimethylamine oxide;

natural surfactants such as saponin, lecithin, soybean  
phospholipid, hydrogenated soybean phospholipid, soybean  
lysophospholipid, hydrogenated soybean lysophospholipid, yolk  
lecithin, hydrogenated yolk lysophosphatidylcholine,  
15 phosphatidylcholine, phosphatidylethanolamine,  
phosphatidylserine, sphingophospholipid, sphingomyelin,  
ganglioside, bile acid, cholic acid, deoxycholic acid, sodium  
cholate, sodium deoxycholate, spiculisporic acid, rhamnolipid,  
trehalose lipid, sophorolipid and mannosyl erythritol lipid;

20 ultraviolet ray absorbers such as: para-aminobenzoic acid  
derivatives such as para-aminobenzoic acid, ethyl  
para-aminobenzoate, glyceryl para-aminobenzoate, amyl  
para-dimethyl aminobenzoate and 2-ethylhexyl para-dimethyl  
aminobenzoate; cinnamic acid derivatives such as benzyl cinnamate,  
25 mono-2-ethyl hexanoate glyceryl dipara-methoxycinnamate, methyl  
2,4-diisopropyl cinnamate, ethyl 2,4-diisopropyl cinnamate,  
potassium para-methoxycinnamate, sodium para-methoxycinnamate,  
isopropyl para-methoxycinnamate, 2-ethylhexyl  
para-methoxycinnamate, 2-ethoxyethyl para-methoxycinnamate and  
30 ethyl para-ethoxycinnamate; urocanic acid derivatives such as  
urocanic acid and ethyl urocanate; benzophenone derivatives such

as 2,4-dihydroxybenzophenone,  
2,2',4,4'-tetrahydroxybenzophenone, sodium  
2-hydroxy-4-methoxy-5-sulfobenzophenone,  
2-hydroxy-4-methoxybenzophenone-5-sulfonate,  
5 2-hydroxy-4-methoxybenzophenone,  
2,2'-dihydroxy-4,4'-dimethoxybenzophenone and sodium  
2,2'-dihydroxy-4,4'-dimethoxy-5-sulfobenzophenone; salicylic  
acid derivatives such as ethylene glycol salicylate,  
salicylate-2-ethylhexyl, phenyl salicylate, benzyl salicylate,  
10 p-tert-butylphenyl salicylate, homomenthyl salicylate and  
salicylate-3,3,5-trimethylcyclohexyl;  
2-(2'-hydroxy-5'-methoxyphenyl)benzotriazole and  
4-tert-butyl-4'-methoxybenzoyl methane;  
powders and color materials such as: kaolin, silicic  
15 anhydride, magnesium aluminum silicate, sericite, talc, boron  
nitride, mica, montmorillonite, hemp cellulose powder, wheat starch,  
silk powder, maize starch; natural dyes such as nitro dyes, azo  
dyes, nitrosodyes, triphenylmethane dyes, xanthene dyes, quinoline  
dyes, anthraquinone dyes, indigo dyes, pyrene dyes, phthalocyanine  
20 dyes, flavonoid, quinone, porphyrin, water soluble annatto, sepia  
powder, caramel, guaiaculene, gardenia blue, gardenia yellow,  
cochineal, shikonin, sodium copper chlorophyllin, paprika dye,  
safflower red, safflower yellow, laccaic acid and riboflavin  
butyrate ester; carbon black, yellow iron oxide, black iron oxide,  
25 red iron oxide, iron blue, ultramarine blue, zinc oxide, chromium  
oxide, titanium oxide, black titanium oxide, zirconium oxide,  
chromium hydroxide, alumina, magnesium oxide, barium sulfate,  
aluminum hydroxide, calcium carbonate, lithium cobalt titanate,  
manganese violet and pearl pigment.  
30 plant extracts such as Angelica keiskei extract, Uncaria  
gambir extract, avocado extract, sweet hydrangea leaf extract,

Gynostemma pentaphyllum makino extract, Althaea officinalis extract, Arnica montana extract, oil soluble Arnica montana extract, almond extract, aloe extract, Japanese styrax benzoin extract, Ginkgo biloba extract, Stinging nettle extract, Orris rhizome root extract, fennel extract, turmeric extract, dog rose fruit extract, Echinacea leaf extract, Scutellaria root extract, Phellodendron bark extract, Japanese captis extract, barley extract, okura extract, Hypericum perforatum extract, oil soluble Hypericum perforatum extract, Lamium album extract, oil soluble Lamium album extract, Ononis spinosa root extract, Nasturtium officinale extract, orange extract, orange flower water, seaweed extract, persimmon tannin, pueraria root extract, Japanese valerian extract, cattail extract, Chamomile (matricaria) extract, oil soluble Chamomile (matricaria) extract, Chamomile (matricaria) distillate, Avena sativa (oat) kernel extract, carrot extract, oil soluble carrot extract, carrot oil, Artemicia capillaris extract, Glycyrrhiza glabra (licorice) extract, powdered Glycyrrhiza glabra (licorice) extract, Glycyrrhiza glabra (licorice) extract flavonoid, cantharides tincture, raspberry extract, kiwi extract, cinchona extract, cucumber extract, apricot kernel extract, quince seed extract, gardenia florida extract, Sasa albomarginata extract, Sophora root extract, walnut shell extract, Citrus paradisi (grapefruit) extract, Clematis vitalba leaf extract, black sugar extract, chlorella extract, mulberry bark extract, Cinnamon bark extract, Gentian extract, Geranium herb extract, black tea extract, Nuphar extract, burdock root extract, oil soluble burdock root extract, wheat germ extract, hydrolyzed wheat powder, rice bran extract, fermented rice bran extract, Symphytum officinale (comfrey) extract, Asiasarum root extract, Crocus sativus (saffron) extract, Saponaria officinalis extract, oil soluble salvia extract, Crataegus cuneata fruit extract, Zanthoxylum fruit extract,

Lentinus edodes extract, powdered Lentinus edodes extract,  
Rehmannia root extract, Lithospermum root extract, oil soluble  
Lithospermum root extract, Perilla herb extract, linden extract,  
oil soluble Tilia europaea extract, Filipendula extract, Peony  
5 root extract, Coix lacryma-jobi extract, ginger extract, oil  
soluble ginger extract, ginger tincture, Acorus calamus root  
extract, Betula pendula (birch) extract, oil soluble Betula alba  
(birch) extract, Betula pendula (birch) sap, Lonicera japonica  
extract, Equisetum arvense extract, oil soluble Equisetum arvense  
10 extract, scordinin, stevia extract, ivy extract, Crataegus  
oxyacanthaha (whitethorn) extract, sambucus extract, Juniperus  
communis extract, Achilleamilefolium extract, oil soluble Achillea  
milefolium extract, Mentha piperita (peppermint) extract, Salvia  
officinalis (sage) extract, oil soluble Salvia officinalis (sage)  
15 extract, Salvia officinalis (sage) water, Malva Sylvestris (mallow)  
extract, Apium graveolens (celery) extract, Cnidium officinale  
extract, Cnidium officinale water, Swertia herb extract, Glycine  
max (soybean) extract, Jujube extract, thyme extract, green tea  
extract, tea leaf dry distilled solution, tea seed extract, clove  
20 extract, Citrus unshiu peel extract, Camellia japonica extract,  
Centella asiatica extract, oil soluble walnut extract, duku extract,  
Terminalia sericea extract, Capsicum tincture, Japanese angelica  
root extract, oil soluble Japanese angelica root extract, Japanese  
angelica root water, Calendula officinalis flower extract, oil  
25 soluble Calendula officinalis flower extract, soy milk powder,  
peach seed extract, Bitter orange peel extract, Houttuynia cordata  
extract, Solanum lycopersicum (tomato) extract, Potentilla  
tormentilla Schrk (Rosaceae) extract, fermented soybeans extract,  
Ginseng extract, oil soluble Ginseng extract, Allium sativum  
30 (garlic) extract, wild rose extract, oil soluble wild rose extract,  
malt extract, malt root extract, Ophiopogon tuber extract, parsley

extract, rye leaf juice concentrate, peppermint distillate, witch hazel distillate, witch hazel extract, rose extract, parietaria extract, Isodonis japonicus extract, Eriobotrya japonica leaf extract, oil soluble Eriobotrya japonica leaf extract, coltsfoot extract, hoelen extract, Ruscus aculeatus root extract, powdered Ruscus aculeatus root extract, grape extract, grape leaf extract, grape water, Hayflower extract, Luffa cylindrica fruit extract, Luffa cylindrica fruit water, Carthamus tinctorius (safflower) extract, oil soluble Tiliaplatyphyllos extract, linden distillate, 5 Paeonia suffruticosa (peony) extract, Humulus lupulus (hops) extract, oil soluble Humulus lupulus (hops) extract, pine extract, Silybum marianum (milk thistle) extract, Aesculus hippocastanum (horse chestnut) extract, oil soluble Aesculus hippocastanum (horse chestnut) extract, Sapindus mukurossi extract, Melissa officinalis (balm mint) extract, Melilotus officinalis (melilot) extract, Prunus persica (peach) leaf extract, oil soluble Prunus persica (peach) leaf extract, bean sprouts extract, Centaurea cyanus flower extract, Centaurea cyanus flower distillate, Eucalyptus globulus extract, Saxifrage extract, Lilium (lily) extract, Coix 10 seed extract, oil soluble Coix seed extract, Artemisia princeps pampanini extract, Artemisia princeps pampanini water, Lavandula angustifolia (lavender) extract, Lavandula angustifolia (lavender) water, apple extract, Ganoderma lucidum extract, Lactuca sativa (lettuce) extract, lemon extract, Astragalus sinicus extract, Rosa centifolia (rose) flower water, Rosemarinus officinalis (rosemary) extract, oil soluble Rosemarinus officinalis (rosemary) extract, Anthemis nobilis extract and 15 Sanguisorba officinalis extract;

amino acids and peptides such as glycine, alanine, valine, 20 leucine, isoleucine, serine, threonine, phenylalanine, tyrosine, tryptophan, cystine, cysteine, methionine, proline,

hydroxyproline, aspartic acid, asparagine, glutamic acid, glutamine, arginine, histidine, lysine,  $\gamma$ -aminobutyric acid, DL-pyrrolidonecarboxylic acid,  $\epsilon$ -aminocaproic acid, hydrolyzed elastin, water soluble elastin, hydrolyzed collagen, water soluble 5 collagen, casein, glutathione, wheat peptides and soybean peptide;

vitamins and factors acting like a vitamin such as: vitamin A and analogues thereof such as retinol, retinal, retinoic acid, retinol acetate and retinol palmitate; carotenoids such as  $\alpha$ -carotene,  $\beta$ -carotene,  $\gamma$ -carotene,  $\delta$ -carotene, lycopene, 10 zeaxanthin, cryptoxanthin, echinenon and astaxanthin; vitamin B<sub>1</sub> and analogues thereof such as thiamines; vitamin B<sub>2</sub> and analogues thereof such as riboflavin; vitamin B<sub>6</sub> and analogues thereof such as pyridoxine, pyridoxal and pyridoxamine; vitamin B<sub>12</sub> and analogues thereof such as cyanocobalamin; folic acids, nicotinic acid, 15 nicotinamide, pantothenic acids, biotins; vitamin C and analogues thereof such as L-ascorbic acid, sodium L-ascorbate, L-ascorbyl stearate, L-ascorbyl palmitate, L-ascorbyl dipalmitate, L-ascorbyl tetraisopalmitate, disodium L-ascorbate sulfate ester, magnesium L-ascorbyl, sodium L-ascorbyl phosphate, 20 L-ascorbate-2-glucoside and magnesium L-ascorbate-2-phosphate; vitamin D and analogues thereof such as ergocalciferol and cholecalciferol; vitamin E and analogues thereof such as d- $\alpha$ -tocopherol, DL- $\alpha$ -tocopherol, dl- $\alpha$ -tocopherol acetate, dl- $\alpha$ -tocopherol succinate,  $\beta$ -tocopherol,  $\gamma$ -tocopherol and 25 d- $\delta$ -tocopherol; ubiquinones, vitamin K and analogues thereof, carnitine, ferulic acid,  $\gamma$ -oryzanol,  $\alpha$ -lipoic acid and orotic acid; antiseptic agents such as benzoic acid, sodium benzoate, undecylenic acid, salicylic acid, sorbic acid, potassium sorbate, dehydroacetic acid, sodium dehydroacetate, isobutyl 30 paraoxybenzoate, isopropyl paraoxybenzoate, ethyl paraoxybenzoate, butyl paraoxybenzoate, propyl paraoxybenzoate,

benzyl paraoxybenzoate, methyl paraoxybenzoate, sodium paraoxybenzoate methyl, phenoxyethanol, light sensitive dye No. 101, light sensitive dye No. 201 and light sensitive dye No. 401;

5       antioxidizing agents such as butylhydroxyanisole, butylhydroxytoluene, propyl gallate, erythorbic acid, sodium erythorbate, para-hydroxyanisole and octyl gallate;

chelating agents to bind to a metal ion such as trisodium ethylenediamine hydroxyethyl triacetate, edetic acid, disodium edetate, trisodium edetate, tetrasodium edetate, sodium citrate, 10 gluconic acid, phytic acid, sodium polyphosphate and sodium metaphosphate;

moisturizing agents such as hyaluronic acid, sodium hyaluronate, sodium chondroitin sulfate, sodium lactate, sodium pyrrolidone carboxylate, betaine, lactic acid bacteria fermented 15 solution, yeast extract and ceramide;

anti-inflammatory agents such as glycyrrhizic acid, trisodium glycyrrhizinate, dipotassium glycyrrhizinate, monoammonium glycyrrhizinate,  $\beta$ -glycyrrhetic acid, glycerin glycyrrhetinate, stearyl glycyrrhetinate, lysozyme chloride, 20 hydrocortisone and allantoin;

pH adjusting agents such as sodium hydroxide, potassium hydroxide and triethanolamine;

salts such as sodium chloride, potassium chloride, magnesium chloride and sodium sulfate;

25        $\alpha$ -hydroxy acids such as citric acid, glycolic acid, tartaric acid and lactic acid;

whitening agents such as arbutin,  $\alpha$ -arbutin and placenta extract;

30       essential oils such as Archangelica officinalis (angelica) oil, Canangium odoratum (ylang ylang) oil, Canarium luzonicum (elemi) oil, orange oil, Chamomilla recutita (matricaria) oil,

Anthemis nobilis oil, Elettaria cardamom (cardamon) oil, Acorus calamus (calamus) oil, Ferula galbaniflua (galbanum) oil, Cinnamomum camphora (camphor) oil, Daucus carota (carrot) seed oil, Salvia sclarea (clary sage) oil, Citrus paradisi (grapefruit) 5 oil, Eugenia caryophyllus (clove) oil, Cinnamon bark oil, Coriandrum sativum (coriander) oil, Cupressus sempervirens (cypress) oil, Santalum album (sandalwood) oil, Juniperus virginiana (cedarwood) oil, Cympogon nardus (citronella) oil, Cinnamomum zeylanicum (Cinnamon) leaf oil, Jasmine officinale 10 (jasmine) absolute oil, Juniperus communis (juniper Berry) oil, Zingiber officinale (ginger) extract, Mentha spicata (spearmint) oil, Salvia officinalis (sage) oil, cedar oil, Pelargonium graveolens (geranium) oil, Thymus vulgaris (thyme) oil, Melaleuca alternifolia (tea tree) oil, Myristica fragrans (nutmeg) oil, 15 Melaleuca qui.viridiflora (niaouli) oil, Citrus aurantium (neroli) oil, pine oil, Ocimum basilicum (basil) oil, Mentha arvensis oil, Pogostemon patchouli (patchouli) oil, Cymbopogon martini (palmarosa) oil, Foeniculum vulgare (fennel) oil, Citrus bigaradia (petitgrain) oil, Piper nigrum (black pepper) oil, Boswellia carterii (frankincense) oil, Vetiveria zizanoides (vetivert) oil, 20 Mentha piperita (peppermint) oil, Citrus bergamia (bergamot) oil, benzoin oil, Aniba rosaeodora (bois de rose) oil, Origanum majorana (marjoram) oil, mandarin oil, Conumiphora myrrha (myrrh) oil, Melissa officinalis (balm mint) oil, Eucalyptus globulus oil, 25 Citrus junos oil, Citrus aurantifolia (lime) oil, Ravensare aromaticum (ravensare) oil, Lavandula latifolia (lavandin) oil, Lavandula angustifolia (lavender) oil, Tilia vulgaris (linden) oil, lemon oil, lemon grass oil, rose oil, Aniba rosaeodora (rosewood) oil, Rosemarinus officinalis (rosemary) oil and 30 Levisticum officinale (lovage) oil;

terpenes such as limonene, pinene, terpinene, terpinolene,

myrcene and longifeelene;

fragrance, water, and the like.

Furthermore, to the external preparation for skin of the invention may also be added any existing raw material of cosmetics at a general concentration. All raw materials of cosmetics described in, for example, Keshouhin genryou kizyun (Standards of raw materials of cosmetics), second edition, notes, edited by Society of Japanese Pharmacopoeia, 1984 (YAKUJI NIPPO LIMITED.), Keshouhin genryou kizyun-gai seibun kikaku (Standards of raw materials of cosmetics, nonstandard ingredients), under the editorship of Pharmaceutical Affairs Bureau Evaluation and Registration Division, 1993 (YAKUJI NIPPO LIMITED.), Keshouhin genryou kizyun-gai seibun kikakutsuiho (Standards of raw materials of cosmetics, nonstandard ingredient, Supplement), under the editorship of Pharmaceutical Affairs Bureau Evaluation and Registration Division, 1993 (YAKUJI NIPPO LIMITED.), Keshouhin syubetsu kyoka kizyun (Standards of cosmetic classification permission), under the editorship of Pharmaceutical Affairs Bureau Evaluation and Registration Division, 1993 (YAKUJI NIPPO LIMITED.), Keshouhin syubetsu haigou seibun kikaku (Standards of cosmetic classification ingredients), under the editorship of Pharmaceutical Affairs Bureau Evaluation and Registration Division, 1997 (YAKUJI NIPPO LIMITED.), Keshouhin genryou jiten (Dictionary of raw materials of cosmetics), 1991 (Nikko Chemicals Co., Ltd.), Atarashii Keshouhinkinou Sozai 300 (New 300 raw materials having cosmetic functions), 2002 (CMC Publishing Co., Ltd) and the like may be used.

#### BEST MODE FOR CARRYING OUT THE INVENTION

Hereunder, the present invention will be specifically explained with reference to the Examples, however, the present

invention is not limited to these Examples.

Example 1:

Under nitrogen atmosphere, into a sufficiently dried Schlenk tube, 13.0 g of 1,6-anhydro- $\beta$ -D-glucopyranose (manufactured by Tokyo Kasei Kogyo Co., Ltd.), 12.5 ml of dry propylene carbonate (manufactured by Sigma-Aldrich Co.) and 66 mass % of 2-butynyltetramethylene sulfonium hexafluoroantimonate (65.8  $\mu$ l) (manufactured by ASAHI DENKA CO., LTD.) were charged. Then, the Schlenk tube was placed in an oil bath, and the oil bath was heated to 100 °C so as to thoroughly dissolve 1,6-anhydro- $\beta$ -glucopyranose. Subsequently, the oil bath was further heated to 130 °C while stirring, so as to allow polymerization to begin. After 30 minutes' reaction, the polymerization solution was added into methanol to stop the polymerization reaction. After removing the solvent, reprecipitation was repeated with water and methanol. The resultant solution was further dialyzed for purification and freeze-dried to obtain 5.3 g of multi-branched polysaccharide A in white powder. The yield was 41 %. The multi-branched polysaccharide A was subjected to  $^1$ H-NMR and  $^{13}$ C-NMR analyses to confirm the structure. Moreover, the weight average molecular weight of the multi-branched polysaccharide A was 20,000 (light scattering method), and the branching degree was 0.38.

Example 2:

Skin lotions as shown in Table 1 were prepared by a conventional method. Ten females of age 20-30 used these lotions and their feedbacks immediately after applying each lotion and after spending one hour with the lotion applied onto the skin at a humidity of 20 % were shown in Table 2. The results revealed that by using Sample 1-1 containing multi-branched polysaccharide A obtained

in Example 1, the moisture feeling of the skin was preserved from immediately after applying the lotion to the time when the skin became dry, and even after the skin became dry, no taut feeling of the skin occurred.

5

Table 1

Sample	1-1	1-2	1-3
Multi-branched polysaccharide A	0.50%	—	—
Glycogen	—	0.50%	—
1,3-buthylene glycol	5.00%	5.00%	5.00%
Ethylalcohol	5.00%	5.00%	5.00%
Citric acid	0.01%	0.01%	0.01%
Sodium citrate	1.00%	1.00%	1.00%
Methyl paraben	0.20%	0.20%	0.20%
Pure water	88.29%	88.29%	88.79%
	100.00%	100.00%	100.00%

Table 2

Sample	1-1	1-2	1-3
Moisture feeling immediately after applying	9	8	2
Moisture feeling after the skin dried	8	4	0
Taut feeling immediately after applying	0	0	0
Taut feeling after the skin dried	1	6	9

## Example 3:

With respect to three females of age 30-40, the skin lotions shown in Table 1 were applied onto the skin of the flexor aspect of the forearm twice a day, one time in the morning and the other in the evening, for seven days. The moisture levels in the keratin layer were measured and compared on the morning of the eighth day with a conductivity value determined through high-frequency inductance method by using an impedance meter (SKICON-200:manufactured by IBS Co., Ltd.) as an index, and the results were shown in Table 3. According to the results, by using

sample 1-1 containing multi-branched polysaccharide A obtained in Example 1, enhancement in conductivity was observed, which indicated that the moisture in the keratin layer was increased to replenish the skin moisture.

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Table 3

	Before	After 1-1 applied	After 1-2 applied	After 1-3 applied
Conductivity	100	183	175	118

## Example 4:

Skin lotions as shown in Table 4 were prepared by a conventional method and applied in the same manner as in Example 3. The moisture levels in the keratin layer were measured and compared on the morning of the eighth day by using as an index a conductivity value determined through high-frequency inductance method by an impedance meter, and the results were shown in Table 5. According to the results, by using sample 2-1 containing multi-branched polysaccharide A obtained in Example 1, enhancement in conductivity was observed, which indicated that the moisture in the keratin layer was increased to replenish the skin moisture.

Table 4

Sample	2 - 1	2 - 2	2 - 3
Multi-branched polysaccharide A	0.5%	—	—
Glycine	—	0.5%	—
1,3-butylene glycol	9.5%	9.5%	9.5%
Ethyl alcohol	39.6%	39.6%	39.6%
Castor oil	4.9%	4.9%	4.9%
Methylparaben	0.2%	0.2%	0.2%
Pure Water	45.3%	45.3%	45.8%
	100.0%	100.0%	100.0%

Table 5

	Before	After 2-1 applied	After 2-2 applied	After 2-3 applied
Conductivity	100	189	145	125

## Example 5:

Milky lotions as shown in Table 6 were prepared by a conventional method. Ten females of age 20-30 used these lotions and their feedbacks immediately after applying each lotion and after spending one hour with the lotion applied onto the skin at a humidity of 20 % were shown in Table 7. The results revealed that by using Sample 3-1 containing multi-branched polysaccharide A obtained in Example 1, the moisture feeling of the skin was preserved from immediately after applying the lotion to the time when the skin became dry, and even after the skin became dry, no taut feeling of the skin occurred.

Table 6

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Sample	3-1	3-2	3-3
Multi-branched polysaccharide A	1.0%	—	—
Hydroxyethylcellulose	—	0.5%	—
Xanthan gum	—	0.5%	—
Glycerin	8.0%	8.0%	8.0%
1,3-buthylene glycol	2.0%	2.0%	2.0%
Sodium citrate	1.0%	1.0%	1.0%
Polyethylene glycol 50	0.5%	0.5%	0.5%
Methyl paraben	0.2%	0.2%	0.2%
Pure Water	87.3%	87.3%	88.3%
	100.0%	100.0%	100.0%

Table 7

Sample	3-1	3-2	3-3
Moisture feeling immediately after applying	9	8	5
Moisture feeling after the skin dried	7	5	0
Taut feeling immediately after applying	0	0	1
Taut feeling after the skin dried	1	7	6

## Example 6:

Milky lotions as shown in Table 6 were applied in the same manner as in Example 3. The moisture levels in the keratin layer measured on the morning of the eighth day using as an index a conductivity value determined through high-frequency inductance method by an impedance meter, and the results were shown in Table 8. According to the results, by using sample 3-1 containing multi-branched polysaccharide A obtained in Example 1, enhancement in conductivity was observed, which indicated that the moisture in the keratin layer was increased to replenish the skin moisture.

Table 8

	Before	After 3-1 applied	After 3-2 applied	After 3-3 applied
Conductivity	100	192	178	125

## Example 7:

Under nitrogen atmosphere, into a sufficiently dried flask, 1.0 g of multi-branched polysaccharide A and dry pyridine were charged. Then, 11.5 g of leucine ethylester isocyanate was slowly added dropwise and the mixture was allowed to react at 100 °C for 24 hours. After the reaction, the reaction solution was poured into methanol. After the solvent was distilled off, and reprecipitation was repeated with water and methanol. The resultant solution was further dialyzed for purification and freeze-dried to obtain 1.96 g of multi-branched polysaccharide derivative B in white powder. According to the elemental analysis,

the substitution degree of the compound was 2.9.

**Example 8:**

Milky lotions as shown in Table 9 were prepared by a conventional method. Ten females of age 20-30 used these lotions and their feedbacks immediately after applying each lotion and after spending one hour with the lotion being applied onto the skin at a humidity of 20 % were shown in Table 10. The results revealed that by using Sample 4-1 containing multi-branched polysaccharide derivative B obtained in Example 7, the moisture feeling of the skin was preserved from immediately after applying the lotion to the time when the skin became dry, and even after the skin became dry, no taut feeling of the skin occurred.

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Table 9

Sample	4 - 1	4 - 2	4 - 3
Multi-branched polysaccharide derivative B	1.0%	—	—
Hydroxyethylcellulose	—	0.5%	—
Xanthan gum	—	0.5%	—
Glycerin	8.0%	8.0%	8.0%
1,3-butylene glycol	2.0%	2.0%	2.0%
Sodium citrate	1.0%	1.0%	1.0%
Polyethylene glycol-50	0.5%	0.5%	0.5%
Methylparaben	0.2%	0.2%	0.2%
Pure water	87.3%	87.3%	88.3%
	100.0%	100.0%	100.0%

Table 10

Sample	4-1	4-2	4-3
Moisture feeling immediately after applying	9	8	5
Moisture feeling after the skin dried	6	5	0
Taut feeling immediately after applying	0	0	1
Taut feeling after the skin dried	1	7	6

**Example 9:**

Under nitrogen atmosphere, into a sufficiently dried Schlenk tube, 1.7 g of 1,6-anhydro- $\beta$ -D-mannopyranose and 3.5 ml of dry propylene carbonate were charged. Then, the Schlenk tube was 5 placed in an oil bath, and the oil bath was heated to 90 °C so as to thoroughly dissolve 1,6-anhydro- $\beta$ -D-mannopyranose. Subsequently, 66 % by mass (11.4  $\mu$ l) of 10 3-methyl-2-butynyltetramethylenesulfonium hexafluoroantimonate was added to allow polymerization to begin. After 20 minutes' reaction, the polymerization solution was poured into methanol to stop the polymerization reaction. After removing the solvent, reprecipitation was repeated with water and acetone. The resultant solution was further dialyzed for purification and freeze-dried to obtain 1.11 g of multi-branched polysaccharide C in white powder. 15 The yield was 64 %. The multi-branched polysaccharide C was subjected to  $^1$ H-NMR and  $^{13}$ C-NMR analyses to confirm the structure. Moreover, the weight average molecular weight of the multi-branched polysaccharide C was 80,000 (light scattering method), and the branching degree was 0.43.

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**Example 10:**

Milky lotions as shown in Table 11 were prepared by a conventional method. Ten females of age 20-30 used these lotions and their feedbacks immediately after applying each lotion and 25 after spending one hour with the lotion being applied onto the skin at a humidity of 20 % were shown in Table 12. The results revealed that by using Sample 5-1 containing multi-branched polysaccharide C obtained in Example 9, the moisture feeling of the skin was preserved from immediately after applying the lotion 30 to the time when the skin became dry, and even after the skin became dry, no taut feeling of the skin occurred.

Table 11

Sample	5-1	5-2	5-3
Multi-branched polysaccharide derivative C	0.50%	—	—
Glycogen	—	0.50%	—
1,3-butylene glycol	5.00%	5.00%	5.00%
Ethyl alcohol	5.00%	5.00%	5.00%
Citric acid	0.01%	0.01%	0.01%
Sodium citrate	1.00%	1.00%	1.00%
Methylparaben	0.20%	0.20%	0.20%
Pure Water	88.29%	88.29%	88.79%
	100.0%	100.0%	100.0%

Table 12

Sample	5-1	5-2	5-3
Moisture feeling immediately after applying	10	8	2
Moisture feeling after the skin dried	8	4	0
Taut feeling immediately after applying	0	0	0
Taut feeling after the skin dried	0	6	9

## 5 INDUSTRIAL APPLICABILITY

As described above, according to the present invention where a small amount of multi-branched polysaccharide and/or derivatives thereof is blended in an external preparation for the skin, an excellent external preparation for the skin having effects of giving sufficient moisturized feeling and not causing uncomfortable taut feeling to the skin can be provided.